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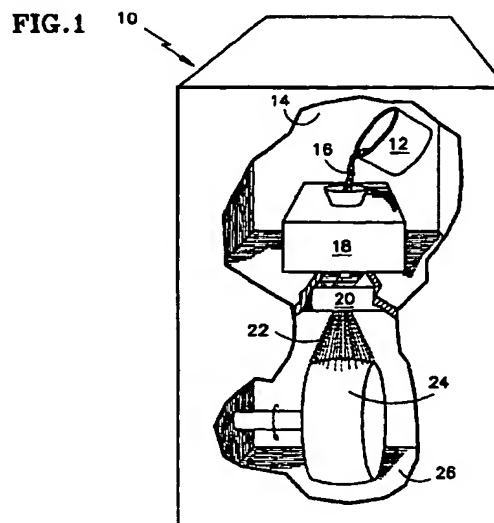
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(54) **Heat treated spray formed superalloy articles and method of making the same**

(57) Heat treated, spray formed articles are disclosed which exhibit crack growth rates and resistance to stress rupture comparable to corresponding, forged articles. The articles are first formed by depositing molten metal droplets, e.g., of a superalloy having a composition in weight percent of about 18-21 w/o Cr, 3.5-5 w/o Mo, 12-15 Co, 2.75-3.25 w/o Ti, 1.2-1.6 w/o Al, 0.01-0.08 w/o Zr, 0.003-0.010 w/o B, balance generally nickel, on a substrate to form a rough article. The articles are HIP'ed and then processed by heat treating, which includes solution, stabilization and precipitation heat treatments. The resultant articles have fine average grain sizes compared to forged and conventionally heat treated material, as well as yield and tensile strengths comparable to forged material. Importantly, the articles also exhibit low crack growth rates and stress rupture resistance, e.g., comparable to forged material, and have an isotropic microstructure. The articles can be used in place of forged articles.



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## Description

[0001] The present invention relates generally to spray formed components, and more particularly to spray formed components having properties comparable to those of corresponding forged components.

5 [0002] Forging has long been used to produce components for demanding applications, e.g., for components which require a combination of high strength and other desired properties such as low crack growth rates and high stress rupture resistance. In the aerospace industry, forging is used to produce rotating and static parts, each of which typically requires a combination of high strength, low crack growth rates and high stress rupture resistance. Such parts can have complex shapes such as blades and vanes, and also include annular-shaped components such as engine cases, 10 flanges and seals

[0003] With particular reference to forging annular-shaped components, a billet of material is obtained having a composition corresponding to the desired composition of the finished component. The billet typically must be specially prepared from ingots of the material. The billet is first pierced, and is then thermomechanically processed, such as by ring-rolling multiple times to transform the billet material into the general component shape. The component may also 15 be heat treated to obtain the combination of desired properties, e.g., a particular level of fatigue crack growth resistance, and then finished, e.g., polished or machined to provide the component with the precise dimensions or features.

[0004] The production of components by forging is an expensive, time consuming process, and thus is typically warranted only for components that require a particularly high level of various properties, e.g., high strength with low crack growth rates and high stress rupture resistance. With respect to obtaining the billets for forging, certain materials 20 require lead times measured in months. During component fabrication, much of the original billet material is removed and does not form part of the finished component, e.g., it is waste. The complexity of the shape of the component produced merely adds to the effort and expense required to fabricate the component. In addition, finished components may still require extensive machining or other finishing. Moreover, in order to operate gas turbine engines at higher temperatures to increase efficiency or power or both, components fabricated from increasingly more advanced alloys are required. Many of these more advanced alloys are increasingly difficult or impossible to forge, which adds further to the 25 cost of the components or renders the components so expensive that it is not economically feasible to exploit certain advances in engine technology, or to utilize particular alloys for some components.

[0005] Spray forming has not previously been used to produce components directly from bulk material, e.g., material in ingot form, which exhibit not only high strength, but also low crack growth rates and high stress rupture resistance. 30 In the case of a nickel base superalloy material having a nominal composition in weight percent of about 19.5 w/o chromium (Cr), 4.3 w/o molybdenum (Mo), 13.5 cobalt (Co), 3.0 w/o titanium (Ti), 1.4 w/o aluminium (Al), 0.05 w/o zirconium (Zr), 0.006 w/o boron (B), balance substantially nickel and nominal amounts of other elements (sometimes referred to as "Waspaloy"), high strength, low crack growth rates and high stress rupture resistance corresponds to meeting the requirements set forth in Aerospace Material Specification AMS 5707 (Rev. H, publ. Aug. 1994), published by SAE Int'l 35 of Warrendale, PA, and incorporated by reference herein. It is this combination of properties which is produced in accordance with the present invention.

[0006] A typical spray forming apparatus is illustrated in FIG. 1. Metal is provided in ingot form and melted in a crucible 12, preferably in a vacuum melt chamber 14 at low pressure and/or in a non-reactive environment. The molten metal 16 is transferred to a tundish 18, and then passes through an atomizer 20, which utilizes an inert carrier gas such as argon to entrain atomized metal droplets. The atomized material 22 impinges upon and is deposited onto a cooler 40 mandrel or substrate 24 that is located in a spray chamber 26. In order to form an annular component, the mandrel is cylindrical and may be rotated, and the stream of atomized metal and the mandrel may be scanned relative to one another. The metal impinges upon the substrate and previously deposited metal, and solidifies rapidly. Layers of the solidified metal then build upon one another to form the desired article. See, e.g., U.S. Pat. 4,830,084. The article may 45 then be further treated, e.g., by hot isostatic pressing (HIP'ing) and/or thermomechanically processing such as by ring rolling to densify and strengthen the material. Superalloys have been melted and spray formed in this manner to form parts, although such parts as formed lack properties such as high strength, low crack growth rates or stress rupture resistance and thus cannot be employed as formed in demanding applications such as gas turbine engines or other high temperature and pressure environments.

50 [0007] The above described Waspaloy material has been widely employed in producing forged parts for use in demanding applications. As noted above, exemplary parts for gas turbine engines include gas turbine engine cases, flanges and seals, as well as blades and vanes. Once formed, these parts typically must still be machined and heat treated to obtain desired properties. AMS 5707 includes a conventional heat treatment for parts forged from this material and is incorporated by reference herein.

55 [0008] Under AMS 5707, a forged component is heat treated in three steps. The first step includes a solution heat treatment at a temperature of between 1825-1900°F (996-1037°C), for about 4 hours, and then cooling at a rate equivalent to air cooling or faster. The second step includes a stabilization heat treatment at a temperature of about 1550°F (843°C) for about 4 hours, and then air cooling. The third step includes a precipitation heat treatment at a temperature

of about 1400°F (760°C) for about 16 hours. The resulting parts have yield strengths of at least about 110 ksi (0.76 GPa) at room temperature, and exhibit relatively low notch sensitivity and high stress rupture resistance. Accordingly, parts produced by forging Waspaloy and heat treated in accordance with AMS 5707 are suitable for use as gas turbine engine cases, flanges or seals, blades and vanes, as well as other demanding applications. However, forged components also often exhibit significant levels of coarse carbides and other inclusions, the levels of which vary significantly from component to component. Forged components tend to be difficult to machine and inspect. Moreover, precise reproducibility is also a concern - forging does not always result in components having dimensions that are identical from part to part. After inspection, many parts must still be re-worked. As a general rule, it is believed that forged parts must be scrapped or re-worked about 20 % of the time.

**[0009]** In an effort to produce components more repeatably and at less expense, we have spray formed test samples using Waspaloy. As spray formed and HIP'd, these parts do have significant strength, but exhibit high crack growth rates and inferior stress rupture resistance, and it has been believed that such parts need to be thermomechanically processed, e.g., forged or ring-rolled, to obtain these properties. The expense of such an added step has not been attractive.

**[0010]** As noted above, a standard, conventional heat treatment for components composed of forged Waspaloy is set out in AMS 5707. However, it has been found that parts composed of sprayformed Waspaloy HIP'ed and heat treated in accordance with AMS 5707 or other conventional heat treatments exhibit yield and tensile strengths similar to forged, but exhibit relatively inferior crack growth rates, stress rupture resistance and other properties that the components cannot be used in demanding applications when these considerations must be addressed.

**[0011]** According to one aspect of the invention, a metal article is disclosed which is composed of a nickel-base superalloy formed by metal droplets built up on one another, for example by sprayforming. The article is then heat treated to provide the article with crack growth rates and stress rupture resistance comparable to the values for forged components heat treated in accordance with AMS 5707. The article is also typically characterized by material having an isotropic microstructure, but may include flowlines to the extent that the sprayformed articles are used as preforms, i.e., the articles are sprayformed and thermomechanically processed.

**[0012]** The present invention incorporates a spray formed article that is processed to provide high strength, and resistance to stress rupture and crack growth.

**[0013]** According to another aspect of the invention, a method is disclosed for generating a spray formed article composed of nickel-base superalloy that has enhanced stress rupture and crack growth resistance characteristics. The method comprises the steps of: spray forming an article, the article as formed characterized by a porosity of up to about 3 percent by volume; and heat treating the article sufficiently to reduce porosity and provide an article having crack growth rates and stress rupture resistance comparable to the values for forged components heat treated in accordance with AMS 5707.

**[0014]** A preferred embodiment will now be described by way of example only and with reference to the accompanying drawings, in which:

FIG. 1 is a schematic view, partially broken away, illustrating an apparatus for spray forming an article;

FIG. 2 is a flow diagram for heat treating articles in accordance with a preferred embodiment of the present invention;

FIG. 3 is a photomicrograph of a spray formed article heat treated in accordance with a preferred embodiment of the present invention;

FIG. 4 is a photomicrograph of microstructure showing forged material after a conventional heat treatment;

FIGS. 5 and 6 are photomicrographs of microstructure of sprayformed articles which have been thermomechanically processed after sprayforming and heat treatment;

FIG. 7 is a graph illustrating 0.5% creep versus applied stress and temperature for articles in accordance with a preferred embodiment of the present invention; and

FIG. 8 is a graph of stress rupture at various temperatures for articles made in accordance with a preferred embodiment of the present invention.

**[0015]** Turning to FIG. 1, a sprayformed HIP'd and heat treated article in accordance with the present invention is first spray formed, in a manner known in the art. See, e.g., U. S. Pat. No. 4,515,864 to Singer entitled "Solid Metal Articles From Built Up Splat Particles", and 3,900,921 to Brooks entitled "Method and Apparatus for Making Shaped Metal Articles From Sprayed Metal or Metal Alloy". With respect to the preferred material for which the present invention is employed, the material has a broad composition (in weight percent) of about 18-21 Cr, 3.5-5 Mo, 12-15 Co, 2.75-3.25 Ti, 1.2-1.6 Al, 0.01-0.08 Zr, 0.003-0.010 B, balance generally Ni; more preferably about 19.5 Cr, 4.3 Mo, 13.5 Co, 3.0 Ti, 1.4 Al, 0.05 Zr, 0.006 B, balance essentially nickel and nominal amounts of other elements (the material is sometimes referred to as "Waspaloy" and is used so herein). The material may also include about 0.04-0.075 C, up to about 0.15 Mn, up to about 0.175 Si, up to about 0.01 S, up to about 0.02 P, up to about 2.25 iron, up to about 0.15 Cu, up to

about 0.00075 Pb, up to about 0.000035 Bi, up to about 0.0005 Ag, up to about 0.01 O, up to about 0.01 N. Briefly, the articles are spray formed and HIP'ed and heat treated in accordance with the present invention, as described further below. Resulting articles are comparable to forgings, with respect to yield and tensile strengths at room temperature and elevated temperatures (e.g., up to at least about 1300°F (704°C)), and also low crack growth rates and high stress rupture resistance - all at significantly less expense, waste, effort and substantially reduced lead times compared to forging.

**[0016]** As discussed above, metal to be used in spray forming is provided, e.g., in ingot form, by melting an elemental mix, by re-melting scrap material or by other manner. The material is melted in a crucible 12, which preferably is positioned in a vacuum melt chamber 14 maintained at low pressure and/or in a non-reactive environment. The molten metal 16 is transferred to a tundish 18, and then passes through an atomizer 20, which utilizes an inert carrier gas such as argon to entrain the atomized metal. The atomized material 22 is directed towards a cooled mandrel or substrate 24 located in a spray chamber 26, which is preferably maintained at low pressure and/or in a non-reactive environment. In order to form an annular component, the mandrel is cylindrical and may be rotated, and the stream of atomized metal and the mandrel may be scanned relative to one another. The metal impinges upon the substrate first and then upon previously deposited metal, and solidifies rapidly, thus providing a finer grain size than forgings. Layers of the solidified metal build up to form the desired article. While an article fabricated from Waspaloy is described, those skilled in the art will recognize that articles made from other materials may also be sprayformed and thermomechanically processed, HIP'ed and heat treated in accordance with preferred embodiments of the present invention. In addition, those skilled in the art will also recognize that there are other methods of depositing molten or semi-molten droplets of material on a substrate with equal effect, such as plasma spraying in a low pressure or vacuum environment which could be employed to form the article.

**[0017]** While the particular spray forming parameters are not believed to be critical to the present invention, we prefer that the droplets are smaller rather than larger, and more preferably on the order of about 10-10,000 microns in diameter. We also prefer that the droplets be applied at a temperature that is lower rather than higher. The droplets preferably should be no hotter than necessary to remain in a semi-molten state until impingement upon the substrate and previously deposited material, but hot enough so as not to substantially solidify prior to impingement. The velocity of the droplets must be fast enough to deliver the droplets in a molten state but slow enough so that the droplets are able to adhere to the substrate and previously deposited droplets. The distance between the spray nozzle and the substrate may also be adjusted, as may the rate at which the material is deposited.

**[0018]** Spray formed articles, as formed, are characterized by the presence of porosity, typically about 1-3 percent by volume (v/o). In contrast, forged articles exhibit no porosity. Porosity tends to reduce the strength of an article. The spray formed articles are treated to densify the material. With reference to FIG. 2, the articles which have been rough formed by spray forming are preferably first densified by HIP'ing. While the particular HIP'ing parameters vary depending upon to the material being HIP'ed and the degree to which porosity is to be reduced, for spray formed Waspaloy the part is preferably HIP'ed at between about 1,800-2,000°F (982-1093°C) and 15,000-25,000 psi (103 GPa-172 GPa) for about four hours, more preferably in an inert atmosphere such as argon. The pressure and temperature are monitored, e.g., at least once every five minutes, to ensure consistent HIP'ing. While FIG. 2 illustrates any subsequent processing or machining as occurring after the heat treatment, the articles may be machined to final dimensions at any time after HIP'ing.

**[0019]** The articles as spray formed exhibit stress rupture resistance and crack growth rates which are significantly inferior to corresponding forged articles. HIP'ing the articles does not significantly improve those properties. Heat treating these articles using industry standards for forged articles, such as AMS 5707 for Waspaloy, does not restore these properties to forged levels. Accordingly, the articles as spray formed and HIP'd only cannot be used in demanding applications such as gas turbine engines.

**[0020]** In accordance with the present invention, the spray formed and HIP'd articles are heat treated in order to provide a balance of strength, low crack growth rates and high stress rupture resistance, and thereby render articles suitable for use in at least these demanding applications. As discussed further below, the preferred heat treatment includes a solution heat treatment 32, a stabilization heat treatment 34 and a precipitation heat treatment 36. The specific temperatures, times and cooling rates described below will vary according to the particular material being processed. The preferred heat treatment provides a spray formed article having a microstructure that is significantly finer and more uniform than that of conventionally forged material. Compare the microstructure of FIGS. 3 and 4. The articles are also finished 38 (FIG. 2) as needed, e.g., machined. The finishing is preferably but not necessarily performed after HIP'ing.

**[0021]** The solution heat treatment 32 comprises the first portion of the heat treatment, and will vary depending upon the particular material being treated. FIG. 3 is a photomicrograph illustrating the microstructure of an article after the article is heat treated in accordance with the present invention. For the Waspaloy material of the composition generally described in AMS 5707, the part is heated to a solution heat treatment temperature preferably between about 1925-2025°F (1052-1107°C), and preferably at about 1975°F (1080°C) for about 2 hours, and quenched in oil or water.

The combination of solution heat treatment temperature and time is selected to be lower than the temperature and time at which the grain size of the material would grow significantly, as larger grain sizes do not provide the desired properties. We have found that sprayformed material appears to be less susceptible to grain growth at elevated heat treatment temperatures than corresponding forged material, and accordingly the solution heat treatment may be performed at higher temperatures than a corresponding solution heat treatment provided in AMS 5707 for forged articles.

**[0022]** After the solution heat treatment, the part is subjected to a stabilization heat treatment 34, the specifics of which will vary depending upon the particular material being treated. For articles fabricated from Waspaloy, the article is heated to a temperature of between about 1500-1600°F (816-871°C), and preferably about 1550°F (843°C) and held at the stabilization heat treatment temperature for about 4 hours, and then cooled at a rate equivalent to air cooling or faster.

**[0023]** After the stabilization heat treatment and cooling, the part is subjected to a precipitation heat treatment 36, which will vary depending upon the particular material being treated. For Waspaloy, the part is heated to a temperature of between 1350-1450°F (732-788°C), and preferably at about 1400°F (760°C) for at least about 16 hours, followed by cooling at a rate equivalent to air cooling or faster.

**[0024]** As noted above, the illustrated application of the preferred heat treatments enables the production of spray formed articles that have not only good strength, but also have other properties that are comparable to or better than forged components, e.g., low crack growth rates and high stress rupture resistance. Samples of the spray formed Waspaloy HIP'd and heat treated in accordance with a preferred embodiment of the present invention were tested to determine yield and ultimate tensile strengths, as well as ductility. With respect to tensile properties, samples were tested both at room temperature (about 68°F (20°C)) and elevated temperature (about 1200°F (649°C)) held for a period of time prior to testing. The samples were subjected to strain rate of between 0.005 in./in./minute ( $8.3 \times 10^{-5}$  m/m/s) through the yield strength (about 110 ksi (0.75 GPa) at room temperature and 93.5 ksi (0.64 GPa) at 1200°F (649°C)). The following properties were obtained:

Property	Room Temp. (20°C)	1200°F (649°C)
Tensile Strength, min.	160 ksi(1.09 GPa)	140 ksi (0.95 GPa)
Yield Strength, 0.2% offset, min.	110 ksi(0.75 GPa)	93.5 ksi(0.64 GPa)
Elongation in 4D, min.	15%	15%
Reduction in area, min.	18%	18%

**[0025]** The minimum values for these properties may be higher or lower, depending upon the particular application of the part. The above values correspond, for example, to the above mentioned parts such as gas turbine engine cases, flanges and seals. The above properties are designed for specific parts such as engine cases and rings.

**[0026]** The above noted properties are comparable to those for forged material, heat treated in accordance with AMS 5707, which calls for the following properties:

Property	Room Temp. (20°C)
Tensile Strength, min.	160 ksi (1.09 GPa)
Yield Strength, 0.2% offset, min.	110 ksi (0.75 GPa)
Elongation in 4D, min.	15%
Reduction in area, min.	18%

**[0027]** As noted in AMS 5707, the properties for forged material should be comparable whether the samples are tested longitudinally or transversely.

**[0028]** In addition, standard combination smooth and notched stress rupture test specimens (comprising material produced in accordance with preferred embodiments of the present invention), e.g., conforming to ASTM E292, were tested. The specimens were maintained at 1350°F (732°C) and loaded continuously, after generating an initial axial stress of between about 75 ksi (0.51 GPa). The specimens ruptured only after at least 23 hours. The above values for

Waspaloy processed in accordance with preferred embodiments of the present invention are comparable to forged material heat treated in accordance with AMS 5707.

[0029] An example of the subsequent processing mentioned above is ring rolling. Briefly, ring rolling is typically employed for annular articles such as engine cases and seals, and includes heating the article and repeatedly passing the article between a series of rollers to form and enlarge the article to the desired size. FIGS. 5 and 6 (each at about 100x magnification; the grains in FIG. 6 being roughly ASTM 8) illustrate the resulting microstructure of sprayformed articles in accordance with the present invention which are ring rolled to produce moderate reduction and high reduction, respectively.

[0030] We have determined that sprayformed (and ring rolled) Waspaloy articles produced in accordance with preferred embodiments of the present invention are generally characterized by a microstructure similar to that of forged Waspaloy articles, but exhibit less edge cracking and result in significantly less grinding losses during finishing than forged Waspaloy. Moreover, sprayformed, ring rolled Waspaloy exhibits superior strength at room and elevated temperatures. At room temperature, spray formed and ring rolled Waspaloy articles produced in accordance with preferred embodiments of the present invention have a 0.2% yield strength of at least about 140 ksi (0.95 GPa) and more preferably above about 155 ksi (1.06 GPa), and an ultimate tensile strength of at least about 180 ksi (1.26 GPa) and more preferably at least about 200 ksi (1.36 GPa). At elevated temperatures (about 1200°F (649°C)) such articles have a 0.2% yield strength of at least about 90 ksi (0.61 GPa) and more preferably above about 93 ksi (0.63 GPa), and an ultimate tensile strength of at least about 135 ksi (0.92 GPa) and more preferably at least about 140 ksi (0.95 GPa).

[0031] Turning now to FIGS. 7 and 8, forged Waspaloy material prepared in accordance with AMS 5707 has been tested to 0.5% creep for various temperatures and stresses (the dashed lines in FIG. 7), and for stress rupture at various temperatures and stresses (the dashed lines in FIG. 8). We have tested corresponding samples of Waspaloy treated in accordance with preferred embodiments of the present invention, and have determined that such samples meet and typically significantly exceed forged Waspaloy tested under the same conditions, e.g., temperature and stress.

[0032] In addition, samples of sprayformed Waspaloy, HIP'd and heat treated in accordance with preferred embodiments of the present invention are characterized by relatively small grains. As measured by specification ASTM E112, grain sizes are about ASTM 3 (three) and more preferably about ASTM 5 or finer, which is comparable to the grains in corresponding forged material heat treated in accordance with AMS 5707. The microstructure of the finished material is substantially more homogeneous and isotropic in properties than forged material. The microstructure is also characterized by the absence of elemental segregation (in contrast to forgings), unless the material is subsequently plastically deformed, and accordingly sections of the material are typically characterized by an absence of flow lines, i.e., which indicate the direction of plastic flow. Moreover, the finished material exhibits low crack growth rates and good stress rupture resistance in addition to an absence of porosity.

[0033] The present heat treatment is not generally interchangeable with standard heat treatments, such as AMS 5707. As discussed above, standard heat treatments for Waspaloy, such as AMS 5707 do not produce satisfactory results when applied to sprayformed articles. For example, the solution heat treatment in AMS 5707 is significantly cooler than that of the present invention, and the cooling occurs by air rather than quenching. Spray formed articles heat treated in accordance with AMS 5707 exhibit reduced creep resistance compared to corresponding forged articles treated in accordance with AMS 5707.

[0034] In summary, the present invention provides other significant advantages over forgings. Generally, the present invention enables spray forming to be used in the direct production of components that have properties comparable to forging. Parts produced in accordance with the present invention are more consistent, with more homogeneous microstructures. Individual parts exhibit isotropic microstructures, unless the articles are subsequently thermomechanically processed such as by ring rolling. The parts are also characterized by a microstructure lacking segregation, especially relative to forgings. These properties also provide components fabricated in accordance with preferred embodiments of the present invention that are more easily machined and inspected.

[0035] Moreover, the present invention obviates the need to obtain specially-prepared billets of material, and long lead times associated with obtaining billets are therefore minimized or eliminated. The present invention enables bulk material to be converted directly to ready-to-machine or use components. Thus, a substantial portion of the effort, expense and waste associated with forging is substantially reduced or eliminated.

[0036] Spray formed articles processed in accordance with preferred embodiments of the present invention exhibit not only strengths similar to the conventional, forged articles, but also resist crack growth and stress rupture resistance at least as well as forged articles. Moreover, articles prepared in accordance with preferred embodiments of the present invention are manufactured at significantly reduced time and expense. From the standpoint of microstructure, sprayformed articles exhibit more uniform, generally finer grains than forgings, and importantly also exhibit significantly less variability in properties as produced, i.e., the properties of the parts lie within a narrower range than do corresponding forged articles.

[0037] Thus, at least in the illustrated embodiments, it can be seen that the present invention may provide spray

formed articles having properties comparable to properties of corresponding forged articles; which have a balance of strength, crack growth rates and stress rupture resistance comparable to corresponding forged articles; in which crack growth rates of the articles are low and stress rupture resistance of the articles are high; and furthermore provides such a heat treatment to provide articles composed of spray formed Waspaloy with properties comparable to those of corresponding articles forged from Waspaloy.

[0038] While the present invention has been described above in some detail, numerous variations and substitutions may be made without departing from the scope of the invention as defined in the following claims. Accordingly, it is to be understood that the invention has been described by way of illustration and not by limitation.

## Claims

1. A metal article composed of a nickel-base superalloy formed by metal droplets built up on one another and heat treated to have strength, creep resistance and stress rupture resistance comparable to the values for forged components heat treated in accordance with AMS 5707.
2. The article of claim 1, wherein the article is composed of material having an isotropic microstructure.
3. The article of claim 1 or 2, wherein the article has a 0.2% yield strength at room temperature of at least about 100 ksi (0.68 GPa) and at about 1200°F (649°C) of at least about 85 ksi (0.58 GPa).
4. The article of claim 1, 2 or 3, wherein the article has an ultimate tensile strength at room temperature of at least about 150 ksi (1.02 GPa) and at about 1200°F (649°C) of at least about 130 ksi (0.89 GPa).
5. The article of any preceding claim, wherein the material has a composition in weight percent of about 18-21 Cr, 3.5-5 Mo, 12-15 Co, 2.75-3.25 Ti, 1.2-1.6 Al, 0.04-0.075 C, 0.01-0.08 Zr, 0.003-0.010 B, balance generally Ni.
6. The article of claim 5, wherein the balance is further composed of about up to about 0.15 Mn, up to about 0.175 Si, up to about 0.01 S, up to about 0.02 P, up to about 2.25 iron, up to about 0.15 Cu, up to about 0.00075 Pb, up to about 0.000035 Bi and up to about 0.0005 Ag.
7. The article of claim 6, wherein the balance is further composed of up to about 0.01 O, up to about 0.01 N.
8. The article of any preceding claim, wherein the article has a microstructure characterized substantially by grains of a size ASTM 3 or finer, as measured in accordance with ASTM E129.
9. A method of generating a spray formed article composed of nickel-base superalloy and having enhanced strength, creep resistance and stress rupture resistance characteristics, comprising the steps of:
  - spray forming an article, the article as spray formed characterized by a porosity of between about 1-3 percent by volume; and
  - heat treating the article sufficiently to reduce porosity and provide an article having strength, creep resistance and stress rupture resistance comparable to the values for forged components heat treated in accordance with AMS 5707.
10. The method of claim 9, wherein the step of heat treating also provides an article having an isotropic microstructure.
11. The method of claim 9 or 10, wherein the step of heat treating also provides an article having a yield strength at room temperature of at least about 100 ksi (0.68 GPa) and at about 1200°F (649°C) of at least about 85 ksi (0.58 GPa).
12. The method of claim 9, 10 or 11, wherein the article has a tensile strength at room temperature of at least about 150 ksi (1.02 GPa) and at about 1200°F (649°C) of at least about 130 ksi (0.89 GPa).
13. The method of any of claims 9 to 12, wherein the material has a composition in weight percent of about 18-21 Cr, 3.5-5 Mo, 12-15 Co, 2.75-3.25 Ti, 1.2-1.6 Al, 0.04-0.075 C, 0.01-0.08 Zr, 0.003-0.010 B, balance generally Ni.
14. The method of claim 13, wherein the balance is further composed of about up to about 0.15 Mn, up to about 0.175 Si, up to about 0.01 S, up to about 0.02 P, up to about 2.25 iron, up to about 0.15 Cu, up to about 0.00075 Pb, up to about 0.000035 Bi and up to about 0.0005 Ag.



to about 0.000035 Bi and up to about 0.0005 Ag.

15. The method of claim 13 or 14, wherein the balance is further composed of up to about 0.01 O, up to about 0.01 N.

5 16. The method of any of claims 9 to 15, wherein the step of heat treating also provides an article having a microstructure substantially characterized by grains of a size less than ASTM 5, as measured in accordance with ASTM E129.

17. The method of any of claims 9 to 16, wherein the step of heat treating includes the steps of:

10        solution heat treating the article;  
         stabilization heat treating the article; and  
         precipitation heat treating the article.

18. The method of any of claims 9 to 17, further comprising the step of:

15        subsequently thermomechanically processing the article to produce a desired shape.

19. The article of any of claims 1 to 8 or the method of any of claims 9 to 18, wherein the article has an annular shape.

20 20. The article of any of claims 1 to 8 or the method of any of claims 9 to 19, wherein the article is a gas turbine engine component.

21. The article of any of claims 1 to 8, 19 or 20, or the method of any of claims 9 to 20, wherein the article is selected from the group consisting of an engine case, an engine flange, and an engine seal.

25 22. A method of making a nickel-based superalloy article having:

30        a 0.2% yield strength at room temperature of at least 100 ksi (0.68 GPa);  
         a 0.2% yield strength at 1200°F (649°C) of at least 85 ksi (0.58 GPa);  
         a tensile strength at room temperature of at least 150 ksi (1.02 GPa); and  
         a tensile strength at 1200°F (649°C) of at least 130 ksi (0.89 GPa),  
         characterised in that the article is formed by building up droplets of metal on one another, densifying the article  
         and heat treating the article, wherein the heat treatment comprises a solution heat treat, stabilization heat treat  
         and a precipitation heat treat.

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FIG.1

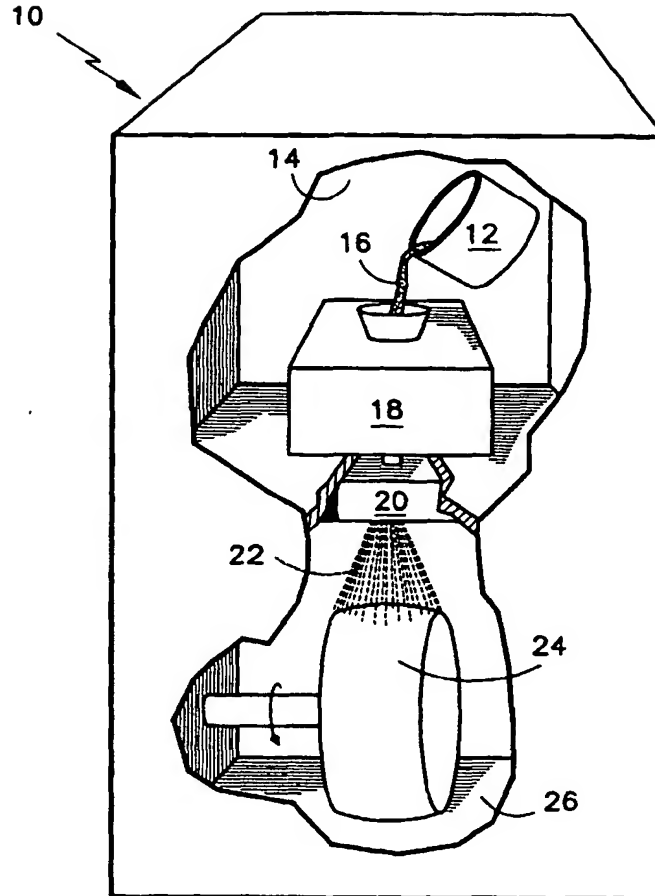


FIG.2

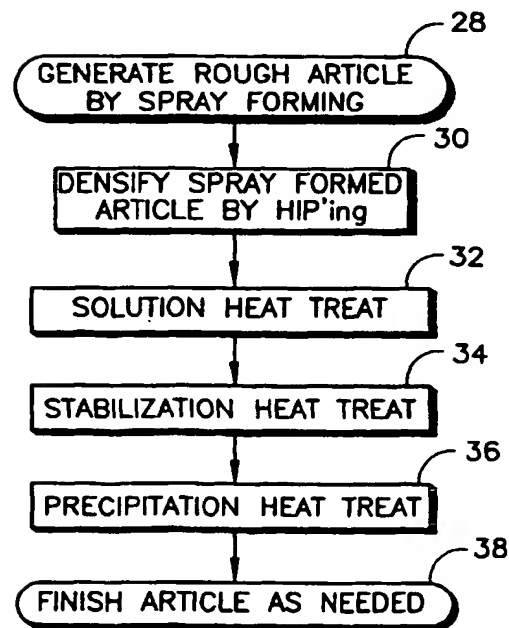


FIG.3

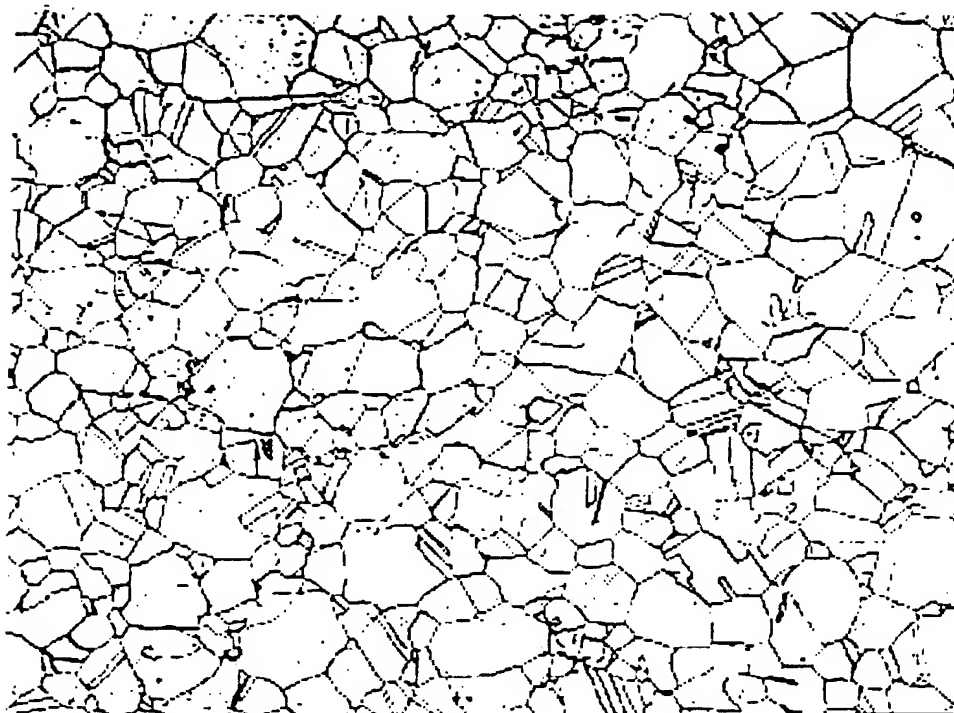
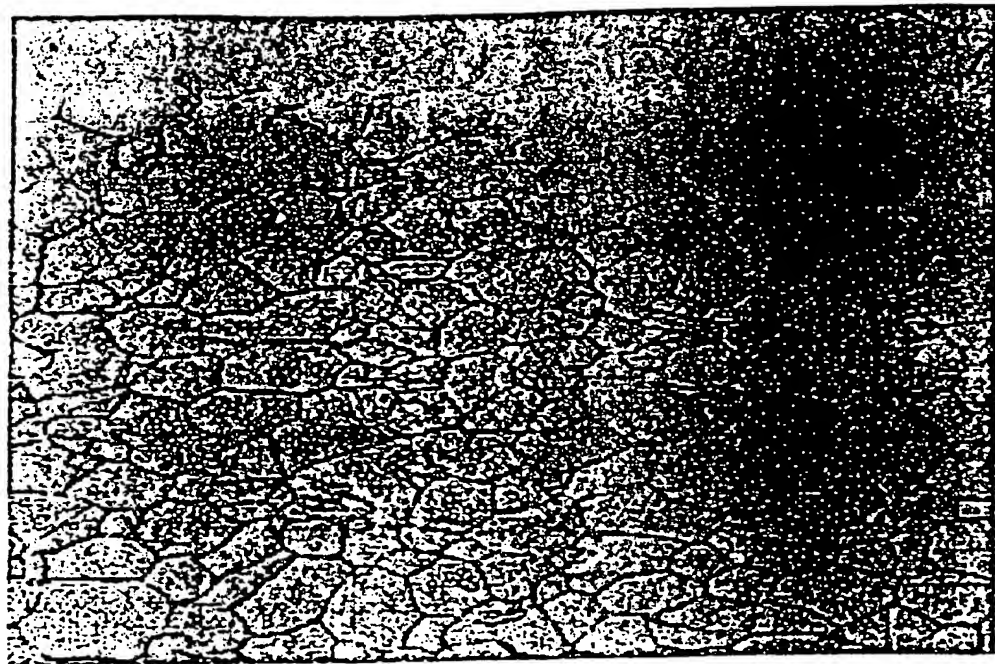


FIG.4



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FIG. 5



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FIG. 6



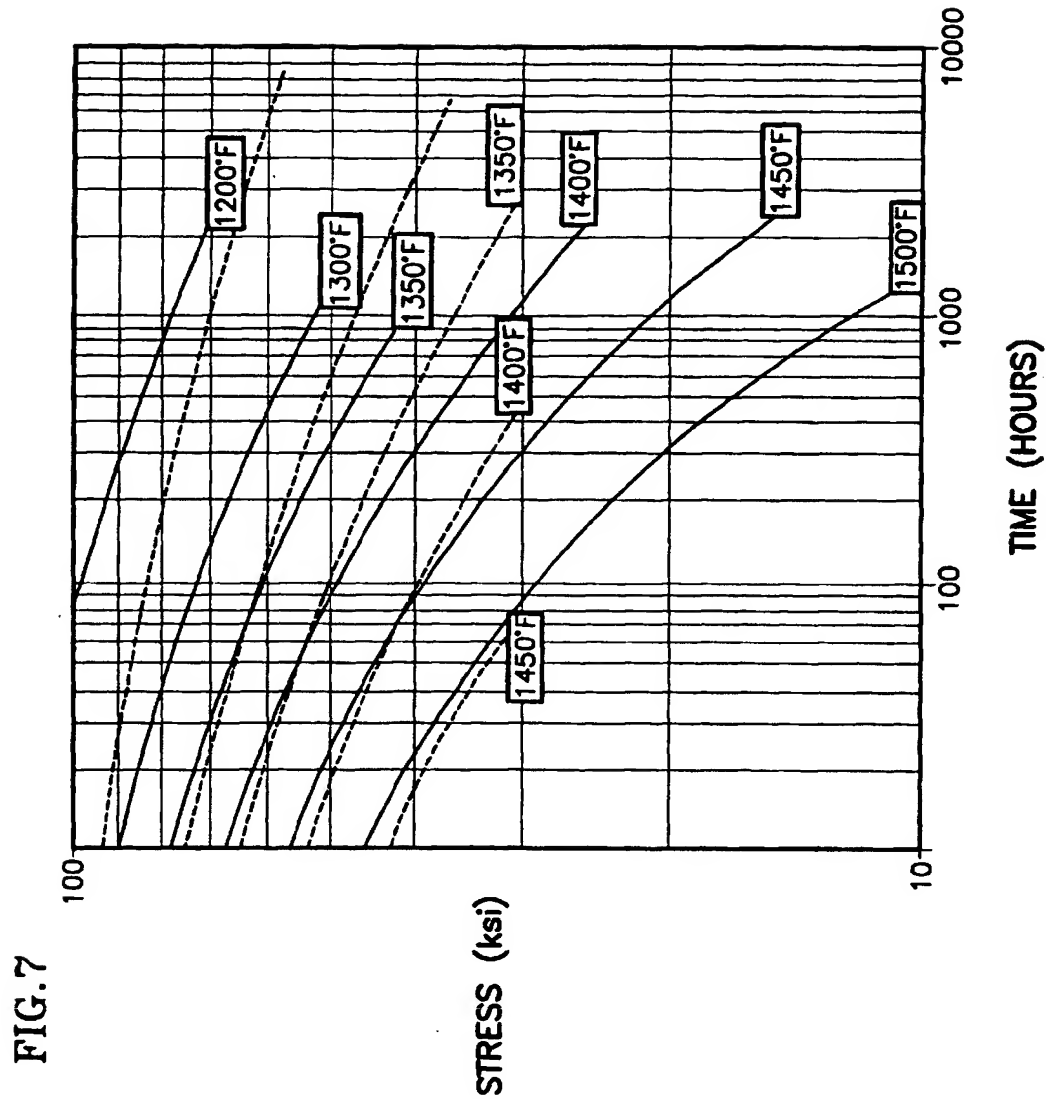
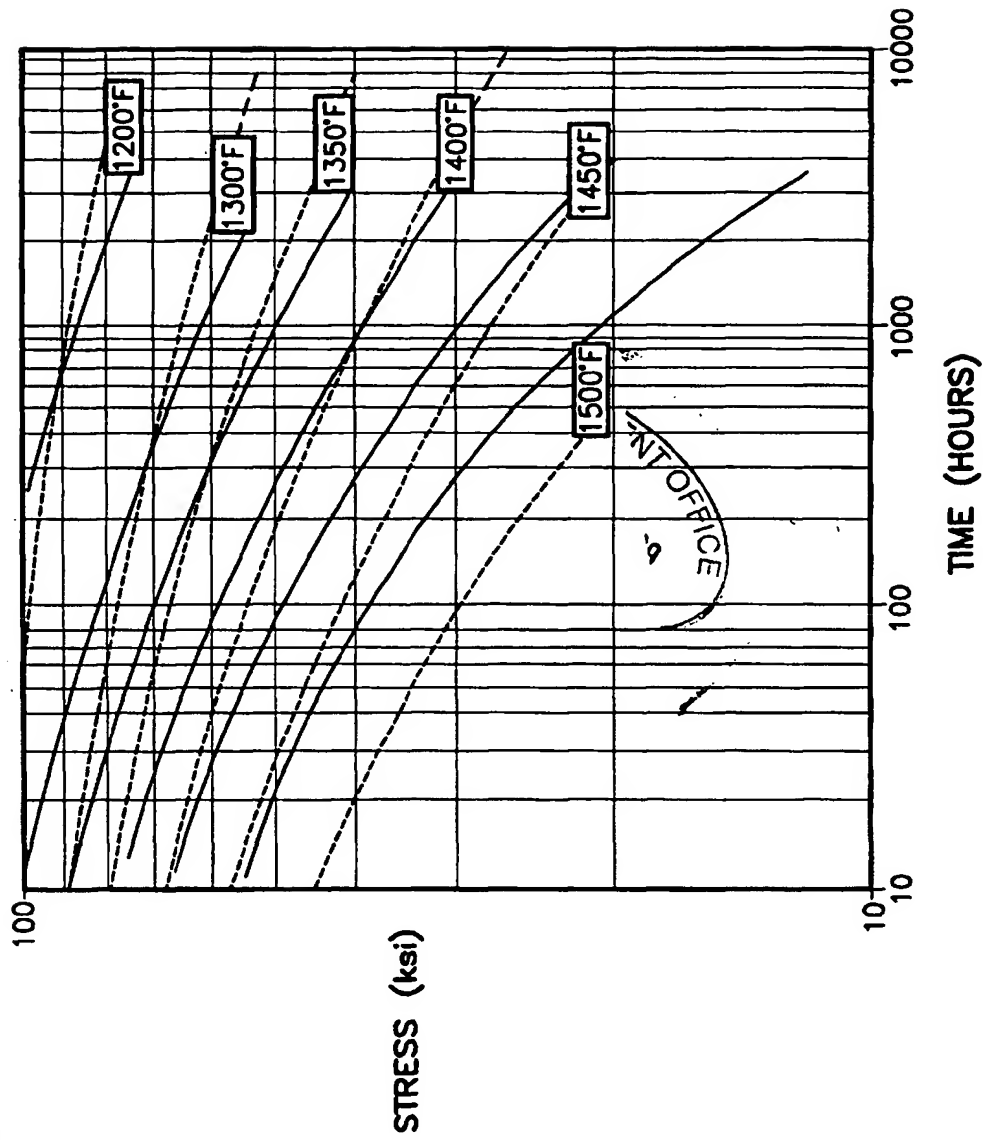


FIG. 8



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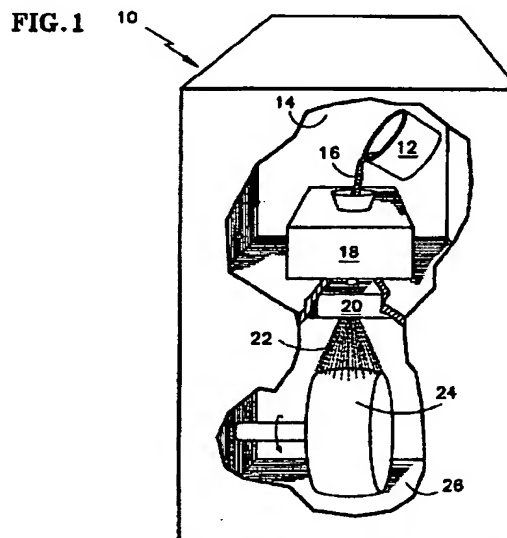
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(30) Priority: **21.12.1998 US 216904**

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(54) **Heat treated spray formed superalloy articles and method of making the same**

(57) Heat treated, spray formed articles are disclosed which exhibit crack growth rates and resistance to stress rupture comparable to corresponding, forged articles. The articles are first formed by depositing molten metal droplets, e.g., of a superalloy having a composition in weight percent of about 18-21 w/o Cr, 3.5-5 w/o Mo, 12-15 Co, 2.75-3.25 w/o Ti, 1.2-1.6 w/o Al, 0.01-0.08 w/o Zr, 0.003-0.010 w/o B, balance generally nickel, on a substrate to form a rough article. The articles are HIP'ed and then processed by heat treating, which includes solution, stabilization and precipitation heat treatments. The resultant articles have fine average grain sizes compared to forged and conventionally heat treated material, as well as yield and tensile strengths comparable to forged material. Importantly, the articles also exhibit low crack growth rates and stress rupture resistance, e.g., comparable to forged material, and have an isotropic microstructure. The articles can be used in place of forged articles.







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# EUROPEAN SEARCH REPORT

Application Number  
EP 99 30 9128

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	CHEMICAL ABSTRACTS, vol. 118, no. 14, 5 April 1993 (1993-04-05) Columbus, Ohio, US; abstract no. 129617, PRICHARD, P. D. ET AL: "Spraycast-X superalloy for aerospace applications" XP002137184 * abstract * -& SUPERALLOYS 1992, PROC. INT. SYMP., 7TH (1992), 205-14. EDITOR(S): ANTOLOVICH, STEPHEN D. PUBLISHER: MINER. MET. MATER. SOC., WARRENDALE, PA , XP002137180 * page 208; figures 3,6; table 1 * * page 212 *	1-22	C23C4/12 C22C19/05
X	CHEMICAL ABSTRACTS, vol. 124, no. 6, 5 February 1996 (1996-02-05) Columbus, Ohio, US; abstract no. 63417, DALAL, R. P. ET AL: "Thermomechanical processing of Spraycast-XTM superalloys" XP002137185 * abstract * -& SPRAY FORM. 2, PROC. INT. CONF. SPRAY FORM., 2ND (1993), 141-53. EDITOR(S): WOOD, JOHN V. PUBLISHER: WOODHEAD PUBLISHING, CAMBRIDGE, UK. , XP002137181 * page 146 *	1-22	<div>TECHNICAL FIELDS SEARCHED (Int.Cl.7)</div> <div>C23C C22C</div>
The present search report has been drawn up for all claims			
Place of search <b>MUNICH</b>		Date of completion of the search <b>9 May 2000</b>	Examiner <b>Ashley, G</b>
<div>CATEGORY OF CITED DOCUMENTS</div> <div> X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document </div> <div> T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons  &amp; : member of the same patent family, corresponding document </div>			

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## EUROPEAN SEARCH REPORT

Application Number  
EP 99 30 9128

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	CHEMICAL ABSTRACTS, vol. 110, no. 4, 23 January 1989 (1989-01-23) Columbus, Ohio, US; abstract no. 27570, PUSCHNIK, H. ET AL: "Spray formed Waspaloy for disk forgings" XP002137186 * abstract * -& PROC. INT. CONF. PM AEROSP. MATER. (1988), MEETING DATE 1987, 14.1-14.7 PUBLISHER: MPR PUBL. SERV. LTD., SHREWSBURY, UK. , XP002137182 ---		
A	CHEMICAL ABSTRACTS, vol. 107, no. 18, 2 November 1987 (1987-11-02) Columbus, Ohio, US; abstract no. 159431, FIEDLER, H. C. ET AL: "The spray forming of superalloys" XP002137187 * abstract * -& J. MET. (1987), 39(8), 28-33 , XP002137183 ---		TECHNICAL FIELDS SEARCHED (Int.Cl.7)
A	GB 2 085 778 A (GEN ELECTRIC) 6 May 1982 (1982-05-06) ---		
A	US 5 584 948 A (HURON ERIC S) 17 December 1996 (1996-12-17) -----		
The present search report has been drawn up for all claims			
Place of search <b>MUNICH</b>		Date of completion of the search <b>9 May 2000</b>	Examiner <b>Ashley, G</b>
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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ON EUROPEAN PATENT APPLICATION NO.**

EP 99 30 9128

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09-05-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 2085778 A	06-05-1982	US 4418124 A	29-11-1983
		CH 657872 A	30-09-1986
		CH 656145 A	13-06-1986
		DE 3139219 A	27-05-1982
		FR 2491365 A	09-04-1982
		IT 1144917 B	29-10-1986
		JP 1628159 C	20-12-1991
		JP 2055493 B	27-11-1990
		JP 57152459 A	20-09-1982
		NL 8104538 A	03-05-1982
		US 4447466 A	08-05-1984
US 5584948 A	17-12-1996	NONE	

EPO FORM P/459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82